

2. Ionic crystals:

We will consider that the cohesive energy is mainly defined by the potential energy of classical particles localized at equilibrium positions. Therefore the lattice energy of a solid which is previously defined will be considered instead. Here the ionic bonding that joins oppositely charged ions is responsible for forming such crystals. Thus the interionic Coulomb interaction and not the dipole-dipole interaction is the dominant interaction for such crystals. However, the short range core-core repulsion due to Pauli principle must also be considered.

Electrostatic or Madelung energy:

Since the main contribution to the binding energy of ionic crystals is electrostatic (or called Madelung energy), which is a long range interaction between ions $-Z_1e$ and Z_2e . But this is attractive for ions of different type or repulsive for ions of the same type. This interaction energy between an ion "i" and other ions "j" whether it is positive or negative is defined as:

$$(U_{ij})_{Coulomb} = \pm \frac{kZ_1Z_2e^2}{r_{ij}}$$

When monovalent Alkali halides are considered then we set $Z_1=Z_2=1$.

The Van der Waal attractive part of this interaction between closed shell ions is similar to that between noble gases and is extremely small in comparison to the Coulomb type of interaction and can be neglected.

The core-core repulsion due to Pauli principle is represented either as the inverse power law:

$$(U_{ij})_{Core-Core} = \pm \frac{C'}{r_{ij}^m}, \text{ where the parameter } C' \text{ will be determined}$$

latter, or as an exponential form (the so-called Born-Mayer

$$\text{potential): } (U_{ij})_{Core-Core} = \lambda e^{-r_{ij}/\rho}.$$

The latter may be the most popular choice. The parameter λ represents the energy strength and ρ represents the range of repulsive interaction. Both λ and ρ are treated as empirical parameters, i.e. constants to be determined from experimental data of lattice constant and compressibility. The sum of all interactions of the i^{th} ion gives:

$$U_i = \sum_{i \neq j} \left(\lambda e^{-r_{ij}/\rho} \pm \frac{e^2}{r_{ij}} \right),$$

$$\text{Or } U_i = \sum_{i \neq j} \left(\frac{C'}{r_{ij}^m} \pm \frac{e^2}{r_{ij}} \right), \text{ where the core-core interaction is written}$$

as the sum of a central field potential.

(Here k is given the value of unity in c.g.s. system).

Note: The value of U_i in NaCl structure does not depend whether the reference ion " i " is a positive or a negative ion.

Thus the total lattice energy $U_{tot} = N U_i$, (where the surface effects are neglected). Here N represents the number of molecules or (ion pair) in a crystal by counting each pair of interactions only once.

Put $r_{ij} = M_{ij}r$, where M_{ij} is a dimensionless number and r is considered here as the nearest-neighbor distance. The total lattice energy can be expressed as:

$$U_{tot} = N \sum_{i \neq j} \left(\lambda e^{-M_{ij}r/\rho} \pm \frac{e^2}{M_{ij}r} \right),$$

and the total energy per ion pair has the

$$\text{form: } u_{tot} = \left(\zeta \lambda e^{-r/\rho} - \frac{\alpha e^2}{r} \right).$$

Here ζ is obtained from the first sum and represents the number of nearest neighbor of any ion, and $\alpha = \sum_{i \neq j} \frac{(\pm)}{M_{ij}}$ is called the

Madelung constant. The latter is positive for a stable crystal.

In a similar manner the total energy per ion pair may have the expression:

$$u_{tot} = \left(\frac{C}{r^m} - \frac{\alpha e^2}{r} \right), \text{ where } C = \sum_{i \neq j} \frac{C'}{M_{ij}^m} \text{ is also obtained from the}$$

first sum.

Note:

It must be noted that NaCl in 3-D solid has the following distances (see figure 25):

- i) Each Na^+ ion has 6 Cl^- ions at nearest neighbor distance r_0 .
- ii) Each Na^+ ion has 12 Na^+ ions at next nearest neighbor distance $\sqrt{2}r_0$.
- iii) Each Na^+ ion has 8 Cl^- ions at third nearest neighbor distance $\sqrt{3}r_0$.

- iv) Each Na^+ ion has 6 Na^+ ions at fourth nearest neighbor distance $2r_o$.

The total lattice energy per ion pair at equilibrium:

The cohesive energy per ion pair can be obtained when the equilibrium separation r_o is determined by minimizing the total energy per ion pair. Thus the parameter λ can be obtained when r_o and ρ are known. Also the parameter C can be determined when r_o and m are known.

The cohesive energy per ion pair (or total lattice energy per ion pair at equilibrium) has either the expression:

$$u_o = E_{Madelung} \left(1 - \frac{\rho}{r_o}\right),$$

Or the expression: $u_o = E_{Madelung} \left(\frac{m-1}{m}\right)$, where the Madelung

energy per ion pair is written as: $E_{Madelung} = -\frac{\alpha e^2}{r_o}$

Notes:

- 1) If the value of ρ is of the order of $0.1r_o$ then such repulsive

interaction $[(U_{ij})_{Core-Core} = \lambda e^{-r_{ij}/\rho}]$ can be considered as a very short range.

- 2) The best method to determine m can be achieved by the experimental measurement of the bulk modulus. If the equilibrium bulk modulus B_o and the equilibrium nearest neighbor separation r_o are known, then we may have the

$$\text{value } m = 1 + \frac{18B_o r_o^3}{|u_{Coul}(r_o)|}, \text{ where } u_{Coul} = -\frac{\alpha e^2}{r_o}.$$

(Solve problem 20.2 in "Solid state physics by N. W. Ashcroft and N. D. Mermin).

Exercise: Consider a line of $2N$ ions of alternating charge $\pm e$ with repulsive potential energy A/r^m between nearest neighbors.

a) Show that at the equilibrium separation $u(r_o) = -\frac{2e^2 \ln 2}{r_o} \left(\frac{m-1}{m}\right)$.

b) Let the crystal be compressed so that $r_o \rightarrow r_o(1-\delta)$. Show that the work done in compressing a unit length of the crystal has the leading term $\frac{C\delta^2}{2}$, where $C = \frac{(n-1)e^2 \ln 2}{r_o}$.

A much better theory!:

The drawback in the above analysis may be avoided when the following are considered:

- 1) The inverse sixth-power of dipole-dipole interaction is included into the theory.
- 2) The zero-point vibrations of the lattice are also employed into the global formulation.

Conclusion:

The fact that the major contribution (may be 90%) of cohesive energy comes from the electrostatic Coulomb interactions among the ions does not change, even with the above mentioned suggested improvements.